Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

PtRu alloy nanostructure electrodes for methanol electrooxidation

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ARTICLE INFO

Article history: Received 28 April 2008 Received in revised form 4 June 2008 Accepted 5 June 2008 Available online 18 July 2008

Keywords: Fuel cells Metals and alloys Nanostructure materials Nanofabrications Catalysis

1. Introduction

Direct methanol fuel cells (DMFCs) using a proton exchange membrane have been considered as suitable power sources for portable applications [1,2]. Because they have a variety of merits such as low operating temperatures, easy to handle a liquid fuel, high energy density of methanol, and applications to microsized fuel cells [3–9]. The excellent catalytic activity of platinum for methanol oxidation, especially at low temperatures, makes this metal electrocatalyst ideal for use as an anode in the DMFCs. However, since pure platinum is rapidly poisoned by intermediates produced during methanol electrooxidation at low temperatures, Pt-based alloy or nanocomposite catalysts with second or third elements need to be designed and synthesized. Among them, PtRu catalyst has been well known as the most effective anode in the DMFCs due to the complete oxidation of methanol to CO₂ via a bifunctional mechanism. According to bifunctional mechanism, the complete oxidation of CO-like intermediates to CO₂ can be promoted by OH group formed on neighbouring Ru at relatively low potential [10-12]. Therefore, the PtRu alloy structure is extremely essential for such an enhanced methanol electrooxidation. In addition, many efforts have been reported to modulate the composition and structure of PtRu nanoparticles by means of physical deposition, chemical synthesis, and

ABSTRACT

In this work, PtRu nanostructure electrodes for methanol electrooxidation were electrodeposited by modulating an electrode potential. The PtRu nanostructures were characterized by scanning electron microscopy, transmission electron microscopy and X-ray diffraction method. To our surprise, it was found that as the electrode potential was increased, the spherical shape of electrode could be transformed into sharp tip formed by PtRu alloy nanoparticles. In particular, the PtRu nanostructure electrode electrodeposited at -0.6 V showed an excellent catalytic activity for methanol electrooxidation due to both bifuctional mechanism and increased active surface area.

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electrochemical method [13–15]. Among them, especially, the electrochemical deposition method has been extensively used because of simple operation, low cost, high purity, and uniform deposition.

In this work, PtRu nanostructure electrodes were electrodeposited with increased potentials. We found that the spherical shape of the electrodes could be transformed into sharp tip with PtRu nanophases with increased electrode potential. The effect of morphology of the electrodes on their electrocatalytic properties was discussed.

2. Experimental

PtRu nanostructure electrodes were electrodeposited on indium tin oxide (ITO) glass in the solution of $0.2 \text{ M} \text{ H}_3\text{BO}_3$, $5 \text{ mM} \text{ H}_2\text{PtCl}_6$, and $0.5 \text{ mM} \text{ RuCl}_3 \cdot \text{3H}_2\text{ O}$ at $25 \,^{\circ}\text{C}$. The electrodeposition was carried out under an applied potential of -0.3, -0.6, -0.9, or -1.2 V for 10 min in a typical electrochemical cell consisting of Pt wire, Ag/AgCl and ITO glass as a counter, reference, and working electrode, respectively. In addition, pure Pt and Ru electrodes were fabricated in the solution of $0.2 \text{ M} \text{ H}_3\text{BO}_3 + 5 \text{ mM} \text{ H}_2\text{PtCl}_6$, and $0.2 \text{ M} \text{ H}_3\text{BO}_3 + 0.5 \text{ mM} \text{ RuCl}_3 \cdot 3\text{H}_2\text{ O}$, respectively.

The morphology and composition of the Pt, PtRu, and Ru electrodes were observed by means of scanning electron microscopy (SEM, JEOL JSM-6360A) and energy dispersive X-ray spectroscopy (EDX). The crystal structures of the Pt, PtRu and Ru electrodes were confirmed by X-ray diffraction (Rigaku X-ray diffractometer equipped with a Cu K α source at 40 kV and 100 mA) and transmission electron microscopy (TEM-Phillips-F20 Electron Microscope at an accelerating voltage of 200 kV).

The conventional electrochemical cell consisting of Pt wire, Ag/AgCl and ITO glass as a counter, reference, and working electrode, respectively, was used to evaluate electrochemical properties and catalytic activity for methanol electrooxidation. Cyclic voltammograms (CVs) of the Pt and PtRu electrodes were obtained in 0.5 M H₂SO₄ and 2 M CH₃OH + 0.5 M H₂SO₄ at a scan rate of 50 mV/s. Chronoamperometry (CA) of the PtRu electrodes were obtained at 0.4 V in 2 M CH₃OH + 0.5 M H₂SO₄.



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^{0925-8388/\$ -} see front matter © 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2008.06.012



Fig. 1. Scanning electron microscopy (SEM) images of Pt electrodes electrodeposited at (a) -0.3 V, (b) -0.6 V, (c) -0.9 V, (d) -1.2 V, PtRu electrodes electrodeposited at (e) -0.3 V, (f) -0.6 V, (g) -0.9 V, (h) -1.2 V, and Ru electrodes electrodeposited at (i) -0.3 V, (j) -0.6 V, (k) -0.9 V and (l) -1.2 V, respectively.



Fig. 2. Low and high resolution transmission electron microscopy (TEM) images of the PtRu electrodes electrodeposited at -0.3 V (a and b) and -0.6 V (c and d).



Fig. 3. (a) An energy dispersive X-ray (EDX) spectrum and (b) composition ratio of the PtRu electrodes.

3. Results and discussion

Fig. 1 shows SEM images of Pt ((a)-(d)), PtRu ((e)-(h)) and Ru ((i)-(l)) electrodes electrodeposited by means of applied potentials. To observe the morphology of the electrodes, the deposition



Fig. 4. X-ray diffraction patterns of PtRu electrodes electrodeposited at (a) -0.3 V, (b) -0.6 V, (c) -0.9 V, (d) -1.2 V, and (e) pure Pt. The asterisk mark represents XRD patterns of ITO glass.



Fig. 5. Cyclic voltammograms (CVs) of Pt and PtRu electrodes deposited at (a) -0.3 V and (b) -0.6 V in 0.5 M $H_2SO_4.$

was carried out under applied potentials of -0.3, -0.6, -0.9, and -1.2 V for 10 min. As shown in Fig. 1(a), (e), and (i), the spherical shape of electrodes is formed at -0.3 V. However, as the potential is increased above -0.6 V, the spherical shape of electrodes is transformed into sharp tip as shown in Fig. 1(b)–(d), (f)–(h) and (j)–(l). In case of PtRu electrodes, the length of the tip is increased with the increased applied potential, as shown in Fig. 1(f)–(h). During the electrodeposition process, platinum and ruthenium ions in the electrolyte are reduced to metal lattice. Simultaneously, the decomposition of water occurs as follows:

$$Pt^{4+} + 4e^- \to Pt^0 \tag{1}$$

$$Ru^{3+} + 3e^- \rightarrow Ru^0 \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (3)

At the higher electrode potentials, the faster water decomposition consequently occurs with an abundant H_2 evolution. The hydrogen bubbles generated in the reaction adhere to the electrode surface; metal nucleation then occurs at high-surface-energy sites on the electrode-bubble interface affected by the local electric field. This enables deposition to extend laterally over the surface covered by the entire bubble. Then, the sharp tip of the electrode radically grows with respect to the configuration of the electric field (Fig. 1(f)-(h)) [16]. It is considered that higher applied potential could produce more tips in the PtRu electrodes due to H_2 evolution on the surface of the electrode. Fig. 2 shows TEM images



Fig. 6. Cyclic voltammograms (CVs) of Pt and PtRu electrodes deposited at (a) -0.3 and (b) -0.6 V for methanol electrooxidation in 2 M CH₃OH + 0.5 M H₂SO₄.

of PtRu electrodes electrodeposited at -0.3 (PtRu-0.3) and -0.6 V (PtRu-0.6). The spherical shape in the PtRu-0.3 is transformed into sharp tip in the PtRu-0.6. As shown in Fig. 2(a) and (b), the PtRu-0.3 seems to be spherical and large polycrystalline structures which are well consistent with SEM images. On the other hand, as shown in Fig. 2(c) and (d), the PtRu-0.6 seems to be sharp tip consisting of PtRu nanoparticles of 4–5 nm. This means that the higher poten-



Fig. 7. Chronoamperometry (CA) of PtRu electrodes for methanol electrooxidation at 0.4 V in 2 M CH₃OH + 0.5 M H₂SO₄.

tials could result in the generation of PtRu nanoparticles caused by fast nucleation and the lateral growth of the nanoparticles on the surface covered by the H_2 bubbles.

Fig. 3 shows EDX data of the PtRu electrodes in Fig. 1(e)-(h). As shown in Fig. 3(b), all the ratios of Pt to Ru in the electrodes is 86:14 at.% and are constant irrespective of applied potentials. In order to confirm crystal structure of the PtRu and Pt electrodes, the XRD patterns were obtained as shown in Fig. 4(a)-(d). The diffraction peaks at around 39.9° , 46.4° and 67.7° correspond to Pt (111), (200) and (220) planes, respectively, with these positions shifted to higher angles compared to those of pure Pt (PCPDF #040802). Assuming alloy formation between Pt and Ru based on substitutional solid solution, such a shift as shown in Fig. 4 is due to the difference of an atomic size between Pt and Ru atom. Also, from the XRD patterns of the PtRu electrodes, it was found that the atomic ratios of Pt to Ru of the electrodes were 80-20 at.% in good agreement with that of EDX analysis. This indicates that all the Pt and Ru elements in the electrodes are alloyed forming homogeneous solid solution within the intended composition.

Fig. 5 shows typical CVs of Pt, PtRu-0.3 and PtRu-0.6. As shown in Fig. 5(a), the Pt and PtRu-0.3 have electrochemical surface areas of 17.71 and 18.14 cm², respectively, measured by absorption sites of hydrogen on platinum surface. On the other hand, as shown in Fig. 5(b), the PtRu-0.6 has much larger electrochemical surface area of 3.99 cm^2 compared to that of 0.27 cm^2 in the Pt electrode. This may be attributed to the increased active surface area of the electrode with the nanostructured tips consisting of PtRu alloy nanoparticles. In the case of the PtRu alloy electrode, the existence of Ru component in the electrode was confirmed by double layer region at the potential range of 0.1-0.6 V thicker than one of pure Pt due to hydrophilic properties of Ru.

Fig. 6 shows CVs of the Pt and PtRu alloy electrodes for methanol electrooxidation in 2 M CH₃OH + 0.5 M H₂SO₄ at 25 °C. As shown in Fig. 6(a), the PtRu-0.3 shows superior catalytic activity to pure Pt, that is, lower onset potential and higher oxidation current density, due to the bifunctional mechanism. In addition, as shown in Fig. 6(b), the PtRu-0.6 shows higher current density for methanol electrooxidation than that of pure Pt. However, compared to the PtRu-0.3, such an excellent catalytic activity the PtRu-0.6 is due to not only bifunctional mechanism but also increased active surface area resulting from the nanostructured tips of the electrode. However, although the higher potential increases active surface area, the highest potential of -1.2 V does not exhibit the most efficient performance in methanol electrooxidation. It is considered that too much hydrogen evolution gives rise to porous films with poor adhesion, thus, deteriorates the stability of electrodeposited electrode. As shown in Fig. 7 using the PtRu electrodes, plots of oxidation current vs. time (CA) were measured in 2.0 M CH₃OH+0.5 M H₂SO₄ at 0.4 V, for 600 s [17,18]. The current measured at PtRu-0.6 is higher than that obtained with PtRu-0.3. By combing CV and CA, we can conclude that PtRu-0.6 represent the best alternative candidates for the DMFC anode catalysts.

4. Conclusion

We found that the growth of nanostructured tips in the PtRu electrodes could be controlled by means of applied potential in electrodeposition method due to H_2 evolution on the surface of the electrode. The PtRu electrode electrodeposited at -0.6 V showed an excellent catalytic activity for methanol oxidation due to both bifuctional mechanism and increased surface area resulting from the nanostructured tips of the electrode. The PtRu nanostructure electrode with the nanostructured tips could be electrodeposited

at an optimum electrode potential and may be promising as an anode in DMFC.

Acknowledgment

This work was supported by Soongsil University Research Fund.

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